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Annealing of some II-IV-V2 crystals in the vapor of volatile constituents

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ABSTRACT

Experiments on annealing of CdGeAs₂- , CdSnAs₂- and ZnGeP₂-crystals in the vapor of volatile constituents were carried out. Conductivity and Hall effect measurements were performed to characterize the modification of electrical properties, caused by the interaction of the crystal with the gas phase during annealing. Literature data and the results of the present work are discussed based on the results of a quasi-chemical analysis. This yielded that the results of annealing depends essentially on both the conditions of the experiment and the initial imperfection of the crystal. The most probable native structural defects becoming apparent under the annealing were the following: for CdSnAs₂ - Sn_{Cd}, V_{As}; for CdGeAs₂ - V_{As}, V_{Cd}, Cd_{Ge}, Ge_{Cd}; for CdSiAs₂ - Si_{As}, V_{As}; for CdSiP₂ - V_{Cd}, V_P; for ZnGeP₂ - Zn_{Ge}, Ge_{Zn}, V_{Zn}, V_P; and for ZnSnP₂ - Zn_{Sn}, Sn_{Zn}, V_{Zn}, V_P.

INTRODUCTION

There is great interest in the ternary compounds II-IV-V₂ (especially CdGeAs₂ and ZnGeP₂) because of their unique properties, among them their use as NLO converters for mid IR range radiation [1,2]. The widespread practical use of these materials is limited by the presence of absorption bands in their transparency range. These absorption bands are linked to deep level native defects [3-6]. For successful suppression of the undesirable influences of these defects on the properties of the material, it is necessary to define their nature. So far there have not been solutions of this task acceptable to all. Experiments on the influence of annealing in the vapor of volatile components on semiconductor electrophysical parameters may be rather informative in this respect. In this work research of such kind applied to n-CdSnAs₂, n- and p-CdGeAs₂ and p-ZnGeP₂ was fulfilled by the method of "frozen reactions".

EXPERIMENTAL RESULTS

In the case of n-CdSnAs₂ the dependence of electron concentrations on vapor pressure appear as curves with a minimum, the depth and position of which on the time axis were defined by defect parameters of the initial sample. This completely agrees with [8]. As it was reported in [9, 10], the hole concentration increased in p-CdGeAs₂ with the lapse of time under annealing in As-vapor and went to saturation at a level about $p \sim 10^{17}$ cm⁻³ under annealing times ~ 150 hours. The electron concentration increased in n-CdGeAs₂ with the lapse of time under annealing in Cd-vapor and went to saturation at a level about $n \sim 10^{18}$ cm⁻³ under annealing times ~ 100 hours [9]. As to ZnGeP₂, it was reported in the work [11] that the hole concentration in the material increased with increase of phosphorus pressure during synthesis

of the compound. According to data of other works, for example, [12-17], annealing in phosphorus vapor reduces the hole concentration (down to p-n conversion of the conductivity type). The results of the present work on annealing in the vapor of volatile components (saturated vapor under pure Cd or As at the temperature of the annealing for $CdGeAs_2$) are presented in Figures 1- 4.

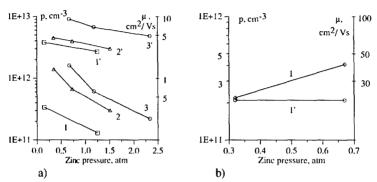


Figure 1. Dependence of concentration (1, 2, 3) and mobility (1', 2', 3') of charge carriers in ZnGeP₂ on pressure of Zn; T_{annealing}, K: 1-1173; 2-1223; 3-1273; t_{annealing}, hours: 1-110; 2-75; 3 - 45; a) material grown from stoichiometric melt under increased P-pressure; b) material grown from a melt containing excess Zn

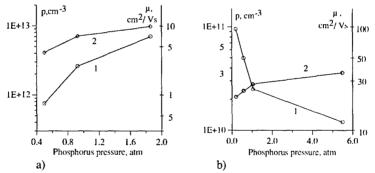


Figure 2. Dependence of concentration (1) and mobility (2) of charge carriers in ZnGeP₂ on pressure of phosphorus; T_{annealing} = 1173 K; t_{annealing} =100 hours; a) material grown from stoichiometric melt under increased P-pressure; b) material grown from a melt containing excess Zn

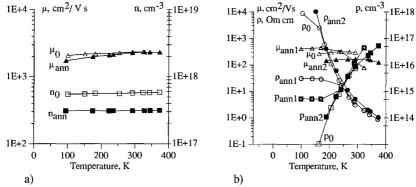


Figure 3. Influence of annealing in As₄ on parameters of CdGeAs₂; empty symbols - temperature dependence of initial parameters (n_0 , p_0 , μ_0 , ρ_0); filled symbols - parameters after annealing at $T_{ann}=773$ K; square - concentration, circle - specific resistance, triangle - mobility; a) n-type, $t_{ann}=384$ hours; b) p-type, $t_{ann1}=190$ hours, $t_{ann2}=384$ hours

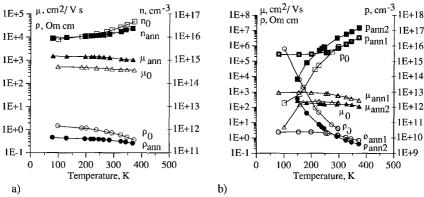


Figure 4. Influence of annealing in cadmium (saturated vapor under pure Cd at 773 K) on electrophysical parameters of CdGeAs₂; empty symbols - temperature dependence of initial parameters (n_0 , p_0 , μ_0 , ρ_0); filled symbols - temperature dependence of parameters after annealing at T=773 K; square - hole concentration , circle - specific resistance, triangle - hole mobility; a) n-type, t_{ann} = 190 hours; b) p-type, t_{ann1} = 30 hours; , t_{ann2} = 90 hours

SCHEME OF QUASI-CHEMICAL ANALYSIS

The processes of formation and interaction of point defects in semiconductors II-IV- V_2 , and also the processes of interaction of the crystals with a gas phase, may be described as a system of quasi-chemical reactions. The following processes were taken into consideration. Formation of Schottky defects (The Kroger designations [7] are used here and further)

$$0 \leftrightarrow V_{A^2}^{\times} + V_{R^4}^{\times} + 2V_{C^5}^{\times} \tag{1}$$

Formation of Frenkel defects

$$\left(A^{2}B^{4}C_{2}^{5} \right)_{cr}^{\times} \leftrightarrow \delta V_{A^{2}}^{\times} + \delta A_{i}^{2^{\times}} + \left(A_{1-\delta}^{2}B^{4}C_{2}^{5} \right)_{cr}^{\times}$$

$$\left(A^{2}B^{4}C_{2}^{5} \right)_{cr}^{\times} \leftrightarrow \delta V_{B^{4}}^{\times} + \delta B_{i}^{4^{\times}} + \left(A^{2}B_{1-\delta}^{4}C_{2}^{5} \right)_{cr}^{\times}$$

$$\left(A^{2}B^{4}C_{2}^{5} \right)_{cr}^{\times} \leftrightarrow \delta V_{C^{5}}^{\times} + \delta C_{i}^{5^{\times}} + \left(A^{2}B^{4}C_{2-\delta}^{5} \right)_{cr}^{\times}$$

$$(2)$$

Formation processes of disorder defects in a common form

$$M_{:i}^{x} + V_{:N}^{x} \leftrightarrow M_{:N}^{x} \tag{3}$$

Interaction processes of crystals with a gas phase using the non-volatility of the elements B⁴ (Si, Ge and Sn) approximation

$$\left(A^{2}B^{4}C_{2}^{5}\right)_{cr}^{\times} \leftrightarrow \delta A^{2^{\times}}(g) + 2\delta/4C_{4}^{5^{\times}}(g) + \left(A_{1-\delta}^{2}B^{4}C_{2(1-\delta)}^{5}\right)_{cr}^{\times}
2/4C_{4}^{5^{\times}}(g) \leftrightarrow 2C_{C_{5}}^{5^{\times}} + V_{A^{2}}^{\times} + V_{B^{4}}^{\times}
A^{2^{\times}}(g) \leftrightarrow A_{A^{2}}^{2^{\times}} + V_{B^{4}}^{\times} + 2V_{C_{5}}^{\times}$$
(4)

Applying the law of mass action to the quasi-chemical reactions and solving the obtained set of equations with respect to concentration of a given point defect under a choice of vapor pressure of one of the volatile components p_{A^2} or p_{C^5} as an independent variable (for tempera-

tures at which component C⁵ exists mainly as four-atom molecules in a gas phase) yields the following expressions

$$[N_{i}^{\times}] = K_{i1} \left(p_{C_{4}^{5}} \right)^{\alpha_{i}} \quad \text{and} \quad [N_{i}^{\times}] = K_{i2} \left(p_{\Lambda^{2}} \right)^{\beta_{i}}, \tag{5}$$

where [N_i^{\times}] is the concentration of neutral defects of i-type, $K_{i1,2}$ are constants at a given temperature, α_i , β_i are constants from the table I

Table I. Exponents α_i or β_i in dependencies of concentrations of neutral native point defects in semiconductors upon pressure of volatile components p_{Λ^2} or $p_{C_1^5}$ respectively

$[N_i^{\times}]$												
α_{i}	1/2	0	-1/4	-1/2	0	1/4	-1/2	-3/4	-1/4	1/2	3/4	1/4
β	-1	0	1/2	1	0	-1/2	1	3/2	1/2	-1	-3/2	-1/2

Applying the law of mass action to the quasi-chemical reactions of ionization of neutral native point defects of the type

$$A_1^{\times} \leftrightarrow A_1 + h \text{ or } D_1^{\times} \leftrightarrow D_1 + e$$
 (6)

yields a set of equations

1.
$$V_{A^{2}} \cdot p = K_{1} \cdot V_{A^{2}}^{\times}$$

2. $V_{B^{4}} \cdot p = K_{2} \cdot V_{B^{4}}^{\times}$

8. $A_{C^{5}}^{2} \cdot p = K_{8} \cdot A_{C^{8}}^{2}$

3. $V_{C^{5}} \cdot n = K_{3} \cdot V_{C^{8}}^{\times}$

9. $B_{C^{4}}^{4} \cdot p = K_{9} \cdot B_{C^{8}}^{4}$

10. $B_{A^{2}}^{4} \cdot n = K_{10} \cdot B_{A^{2}}^{4}$

5. $B_{1}^{4} \cdot n = K_{5} \cdot B_{1}^{4}$

11. $C_{A^{2}}^{5} \cdot n = K_{11} \cdot C_{A^{2}}^{5}$

6. $C_{1}^{5} \cdot p = K_{6} \cdot C_{1}^{5}$

12. $C_{B^{4}}^{5} \cdot n = K_{12} \cdot C_{B^{4}}^{5}$

Adding to the given system written in a common form as

$$A_1' \cdot p = K_1 \cdot A_1^{\times} \text{ or } D_1' \cdot n = K_1 \cdot D_1^{\times},$$

the equation for equilibrium concentration of electrons and holes

$$n \cdot p = K_{14}$$
,

and also the equation of an electroneutrality

$$V_{A^2}^{'} + V_{B^4}^{'} + C_i^{5} + A_{B^4}^{2} + A_{B^4}^{2} + A_{B^4}^{2} + B_{C^5}^{4} + n = V_{C^5}^{'} + A_i^{2} + B_i^{4} + B_{A^2}^{4} + C_{A^2}^{5} + C_{B^4}^{5} + p \; ,$$

and solving the obtained system with respect to concentration of free charge carriers using data from table I, we obtain dependencies of free electron concentration (free hole concentration) upon pressure of volatile components, such as (8) and (9).

$$n^{2} = \frac{K_{3}'p_{C_{4}}^{-1/4} + K_{4}'p_{C_{4}}^{-1/2} + K_{5}' + K_{10}'p_{C_{4}}^{1/2} + K_{11}'p_{C_{4}}^{3/4} + K_{12}'p_{C_{4}}^{1/4} + K_{14}}{K_{1}''p_{C_{5}}^{1/2} + K_{2}'' + K_{6}''p_{C_{5}}^{1/2} + K_{7}''p_{C_{5}}^{-1/2} + K_{8}''p_{C_{5}}^{-3/4} + K_{9}''p_{C_{5}}^{-1/2} + 1} ,$$
 (8)

where $K_{l}' = K_{l} \cdot K_{i}$, $K_{l}'' = K_{l} \cdot K_{i} / K_{l4}$, K_{i} from (5).

$$p^{2} = \frac{K_{1}"p_{C_{4}^{5}}^{1/2} + K_{2}" + K_{6}"p_{C_{4}^{5}}^{1/4} + K_{7}"p_{C_{4}^{5}}^{-1/2} + K_{8}"p_{C_{4}^{5}}^{-3/4} + K_{9}"p_{C_{4}^{5}}^{-1/4} + K_{14}^{2}}{K_{3}"p_{C_{4}^{5}}^{-1/4} + K_{4}"p_{C_{5}^{5}}^{-1/2} + K_{5}' + K_{10}"p_{C_{4}^{5}}^{1/2} + K_{11}"p_{C_{4}^{5}}^{3/4} + K_{12}"p_{C_{5}^{5}}^{1/4} + K_{14}},$$
(9)

where $K_1' = K_1 \cdot K_i$, $K_1'' = K_1 \cdot K_1 \cdot K_1 \cdot K_2$, K_1 from (5).

Analysis of the obtained dependencies of the equilibrium concentration of free charge carriers on pressure yields the following conclusions:

Increase of pressure of the component C⁵ in a system leads to

a) increase in concentration of the donors, connected with disorder, that is BA, CA, CB;

- b) decrease in concentration of the donors, connected with vacancies of an anion and interstitial cations, that is V_C , A_i ;
- c) increase in concentration of acceptors, connected with vacancies in the cation sublattice and interstitial anions, that is V_A , C_i :
- d) decrease in concentration of acceptors, connected with disorder, that is A_B , A_C , B_C . Therefore, it is most probable that the experimentally observed (for example, from measurements of the Hall effect on samples after annealing under high pressure of one of the volatile constituents) shift of carrier concentration in the direction of n-type conductivity with a simultaneous decrease in mobility corresponds to the situation a); the experimentally observed shift of carrier concentration in the direction of p-type conductivity with a simultaneous increase in mobility corresponds to the situation b); the shift in carrier concentration in the direction of p-type with a simultaneous decrease of mobility corresponds to the situation c); the shift in carrier concentration in the direction of n-type with a simultaneous increase of mobility corresponds to the situation d). Designating by \uparrow , the increase in defect concentration and by \downarrow , the decrease in defect concentration, the results of the analysis may be presented as the following schemes:

Table II. The scheme of the correspondence of experimentally observed shift of charge carriers concentration and mobility (a case of primary ion scattering) to a change of concentration of native structural defects after annealing under high pressure of C⁵ or A²

Annealing under high	Observation	Possible cause	Concrete definition
pressure of			
C ⁵	n↑p↓μ↑	A↓	$A_B \downarrow, A_C \downarrow, B_C \downarrow$
C.	n↑p↓μ↓	D↑	$B_A \uparrow$, $C_A \uparrow$, $C_B \uparrow$
C,	n↓p↑μ↑	D↓	$V_{C}\downarrow$, $A_{i}\downarrow$
C,	n↓p↑µ↓	A ↑	$V_A \uparrow, C_i \uparrow$
A^2	n↑p↓μ↑	Α↓	$V_A \downarrow C_i \downarrow$
A^2	n↑p↓µ↓	D↑	$V_{c}\uparrow,A_{i}\uparrow$
A^2	n↓p↑μ↑	D↓	$B_A \downarrow , C_A \downarrow , C_B \downarrow$
A ²	n↓p↑µ↓	A Î	$A_B \uparrow, A_C \uparrow, B_C \uparrow$

QUASI-CHEMICAL ANALYSIS OF EXPERIMENTAL DATA

The results of a change in electrophysical parameters under the heat treatment of some II-IV-V₂ crystals in the vapor of volatile constituents, obtained in the present work and taken from the literature, are analyzed by correlating the experimentally observed shift of charge carrier concentration and mobility (a case of primary ion scattering) to a change of concentration in native structural defects after annealing under high pressure of C⁵ or A² from table III. The results of the analysis are given in tables III and IV.

For $CdSnAs_2$ the presence of two types of donors results from the existence of two time-stages of annealing in vapor of the both volatile components. The first annealing time-stage of $n-CdSnAs_2$ (decrease of electron concentration with sharp increase of electron mobility during annealing in As-vapor) is defined as a fast processes, (for instance, corresponding to the equations 3, 4 of system (7)) and connected mainly with the decrease in concentration of donor vacancies $[V_{As}]$. The second stage changes (increase of electron concentration during annealing in As-vapor) are affected by competitive slower processes (for instance, corresponding to the equations 10 - 12 of system (7)), connected with modifications of disorder defect concentration. Under annealing in Cd-vapor the stages traded places.

Literature data and the results of the present work concerning $ZnGeP_2$ testify that the conditions of the chemical and thermal history of $ZnGeP_2$ crystals (chemical composition of a melt, composition and pressure in a growth technological system etc.) have much influence on concentrations of native structural defects and, because of that, on properties and behavior of $ZnGeP_2$ under further treatments. As follows from figures 1, 2 and from the analysis the crystals $ZnGeP_2$ with different "previous history" have a different ensemble of native structural defects and react differently on an annealing in vapor of volatile components.

For $ZnGeP_2$, the presence of both vacancies (in the present work for $ZnGeP_2 < P>$, when $[V_P]$, probably less than equilibrium concentration for conditions of annealing in Zn-vapor) and disorder defects in the cation sublattice (in the present work for $ZnGeP_2 < Zn>$) were observed.

For CdGeAs₂ the presence of at least two native acceptors has been observed in experiments utilizing radiation damage, magnetic resonance and thermal admittance spectroscopy [20]. As follows from Figures 3, 4 the annealing of n-CdGeAs₂ in both As atmosphere and Cd atmosphere, yielded a diminution of electron concentration. In the first case it was accompanied by a diminution of mobility (u), in the second case it was accompanied by magnification of μ . In the approximation of the scheme used in table I, it corresponds to 1) magnification of concentration V_{Cd} (and, probably, As_i), 2) diminution of concentration of disorder defects such as Ge_{Cd}. We note that annealing in Cd vapor, carried out by the authors of work [9], on n-CdGeAs₂ at T_{anneal} =400 °C, led to (from ~2·10¹⁶ cm⁻³ to ~8·10¹⁷ cm⁻³) the increase in the electron concentration. Probably, the less than 100 °C annealing temperature in experiment [9] was the reason for the smaller activity of disorder defects. The annealing processes were defined by an extreme modification of the concentration of vacancies and led to a sharp increase in electron concentration due to a lack of a competing process, giving an opposite outcome. In the annealing of p-CdGeAs2, a simultaneous course of several competing processes is also observed. The initial annealing stage (30 hours in As4 vapour) gave p-n conversion of conductivity of samples under study (from p $\sim 7 \cdot 10^{15}$ cm⁻³, $\mu \sim 290$ cm²/V·s to n $\sim 8 \cdot 10^{15}$ cm⁻³, $\mu \sim 2800 \text{ cm}^2/\text{V} \cdot \text{s}$ at T _{meas} $\sim 290 \text{ K}$, and n $\sim 5 \cdot 10^{15} \text{ cm}^{-3}$, $\mu \sim 3900 \text{ cm}^2/\text{V} \cdot \text{s}$ at T _{meas} $\sim 95 \text{ K}$). Using the same approximations as in table I, the concentration of disorder defects ($Cd_{Ge} \downarrow$, Ge_{Cd} \uparrow) increases, or it is explained by uncontrollable doping of the samples (for example, by O_2). The outcomes of long annealing of p-CdGeAs, in As₄ are presented in figure 3 b). The increase in hole concentration with respective change in mobility corresponds to a stage of 190 hours of annealing. It can be described by the increase of $[V_{Cd}]$ and the decrease of $[V_{As}]$. The stage of 384 hours is characterized by an outcome (p \downarrow , $\mu \downarrow$). That can mean a prevalence of the first process (Ge_{Cd} 1). Similar experiments on annealing of p-CdGeAs₂ in As₄ vapor were carried out by the authors [9, 10]. In this case the annealing temperature differed less (450 °C [10] and 520 °C [9]). However, the influence of the process, defined by disorder defects, which were observed in the work [9, 10] are lacking. Probably, it is possible to assume, that in this case the initial imperfection of samples under study plays a key role. A different imperfection caused different routes and different times, necessary for reaching an equilibrium condition. From an analysis of the observed modifications of electrophysical parameters, associated with annealing of p-CdGeAs₂ in Cd, we can approximate the influence of processes connected with disorder defects as follows. Such processes as $A_B \uparrow$, $A_C \uparrow$, $B_C \uparrow$ and $B_A \downarrow$, $C_A \downarrow$, C_B ↓ play a defining role. Thus, after annealing of n- and p-CdGeAs₂ under high pressure of the volatile components, we observed the influence of such native defects as V_{Cd}, V_{As}, Cd_{Ge}, Ge_{Cd}. We note that annealing in the vapor of the element A² (Cd) was difficult because of the high chemical activity of the element A² in relation to a surface of crystals A²B⁴C⁵:2. This caused formation of surface layers of a different chemical nature.

Table III. The results of the quasi-chemical analysis of experimental data of the present work and also literary data on annealing in vapour of volatile components for some II-IV-V₂ (The data of the present work are marked by an asterisk)

Compound Annealing		Observed change	Responsible native defects		
	in vapour	5			
CdSnAs ₂	C ⁵	1) n ↓ p ↑ μ ↑ [8],[*]	$V_C \downarrow$, $A_i \downarrow$		
	C ⁵	2) n \uparrow p \downarrow μ \downarrow [8],[*]	$B_A \uparrow, C_A \uparrow, C_B \uparrow$		
	A^2	1) $n \downarrow p \uparrow \mu \uparrow [8],[*]$	$B_A \downarrow , C_A \downarrow , C_B \downarrow$		
	A^2	2) n \uparrow p \downarrow μ \downarrow [8],[*]	$V_{\rm C} \uparrow$, $A_{\rm i} \uparrow$		
CdGeAs ₂	C ⁵	1) n ↓ p↑ μ ↑ [10, 9],[*]	$V_C \downarrow$, $A_i \downarrow$		
	C ⁵	2) n ↓ p ↑ μ ↓ [*]	$V_A \uparrow, C_i \uparrow$		
	C ⁵	3) n↑p↓μ?[*]	$A_B \downarrow, A_C \downarrow, B_C \downarrow$		
			$B_A \uparrow, C_A \uparrow, C_B \uparrow$		
	A^2	1) n↑p↓μ?[10],[*]	$V_C \uparrow$, $A_i \uparrow$ or $V_A \downarrow$, $C_i \downarrow$		
	A^2	2) n ↓ p ↑ μ ↑ [*]	$B_A \downarrow , C_A \downarrow , C_B \downarrow$		
	A^2	3) n ↓ p ↑ μ ↓ [*]	$\begin{array}{c c} A_{B} \uparrow, A_{C} \uparrow, B_{C} \uparrow \\ \hline V_{C} \downarrow, A_{i} \downarrow \end{array}$		
CdSiAs ₂	C ⁵	1) n ↓ p ↑ μ ↑ [11,18]			
	C ⁵	2) n↑p↓μ↑[11]	$A_B \downarrow, A_C \downarrow, B_C \downarrow$		
	A^2	1) n ↑ p ↓ μ ↓ [11,18]	$V_{\rm C}\uparrow$, $A_{\rm i}\uparrow$		
	A ²	2) n ↓ p ↑ μ ↓ [11]	$A_B \uparrow, A_C \uparrow, B_C \uparrow$		
CdSiP ₂	C ⁵	n↓p↑μ?[15]	$V_C \uparrow, A_i \uparrow, V_A \downarrow, C_i \downarrow$		
ZnGeP ₂	C ⁵	n↓p↑μ?[11]	$V_C \uparrow, A_i \uparrow, V_A \downarrow, C_i \downarrow$		
Į.	A^2	n↓p↑μ↑ [12]	$B_A \downarrow , C_A \downarrow , C_B \downarrow$		
1	C ⁵	n↑p↓μ↑ [12]	$A_B \downarrow, A_C \downarrow, B_C \downarrow$		
	A^2	n↓p↑μ? [13-17]	disorder defects		
	C ⁵	n↑p↓μ?[13-17]	disorder defects		
$ZnGeP_2 < P > A^2$		n↑p↓μ↓ [*]	$V_{\rm C} \uparrow$, $A_{\rm i} \uparrow$		
	C ⁵	n↓p↑μ↑ [*]	$V_C \downarrow$, $A_i \downarrow$		
ZnGeP2 <zn></zn>	A^2	n↓p↑μ↓ [*]	$A_B \uparrow, A_C \uparrow, B_C \uparrow$		
	C ⁵	n↑p↓μ↑ [*]	$A_B \downarrow, A_C \downarrow, B_C \downarrow$		
ZnSnP ₂	A^2	1) n ↓ p ↑ μ ↑ [19]	$B_A \downarrow , C_A \downarrow , C_B \downarrow$		
	A^2	2) n↑p↓μ↓[19]	$V_{c}\uparrow$, $A_{i}\uparrow$		
	C ⁵	1) n↑p↓μ↑[19]	$A_B \downarrow, A_C \downarrow, B_C \downarrow$		
	C ⁵	2) n ↓ p ↑ µ ↓ [19]	$V_A \uparrow$, $C_i \uparrow$		

Table IV. The most probable native structural defects in some $A^2B^4C^5_{;2}$ exhibited under heat treatment in vapor of volatile constituents and satisfying to the Hume-Rothery criterion

Compound	CdSnAs ₂	CdGeAs ₂	CdSiAs ₂	CdSiP ₂	ZnGeP ₂	ZnSnP ₂
Defects	Sn_{Cd}, V_{As}	$V_{As}, V_{Cd},$	Sias, Vas	V_{Cd}, V_P	Zn _{Ge} , Ge _{Zn} ,	Zn_{Sn} , Zn_P , Sn_{Zn} ,
	1	Cd _{Ge} , Ge _{Cd}			V_{Zn}, V_P	P_{Z_n}, V_{Z_n}, V_P

CONCLUSIONS

- 1. Experiments on annealing of CdGeAs₂-, CdSnAs₂- and ZnGeP₂-crystals in the vapor of volatile constituents were carried out. Conductivity and Hall effect measurements were performed to characterize the modification of electrical properties, caused by interaction of the crystal with the gas phase during the annealing.
- 2. A scheme for correlating the experimentally observed shifts of charge carrier concentration and mobility (a case of primary ion scattering) to a change in concentration of native structural defects after annealing under high pressure of C⁵ or A², based on quasi-chemical analyses was presented.
- 3. The literature data and results of the present work on the annealing were discussed based on the results of a quasi-chemical analysis.
- 4. It was noted that the outcomes of the annealing essentially depend on both the initial imperfections of the crystal and the conditions of the experiment as they define the route and time of reaching an equilibrium..
- 5. For some II-IV-V₂ the most probable native structural defects becoming apparent under heat treatment in the vapor of volatile constituents and satisfying to the Hume-Rothery criterion were the following: For CdSnAs₂ Sn_{Cd}, V_{As}; for CdGeAs₂ V_{As}, V_{Cd}, Cd_{Ge}, Ge_{Cd}; for CdSiAs₂ Si_{As}, V_{As}; for CdSiP₂ V_{Cd}, V_P; for ZnGeP₂ Zn_{Ge}, Ge_{Zn}, V_{Zn}, V_P; for ZnSnP₂- Zn_{Sn}, Sn_{Zn}, V_{Zn}, V_P.

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REFERENCES

- N.A.Goryunova, S.Mamaev, V.D.Prochukhan, Properties of CdSnAs₂ semiconductor an electronic analog of InAs, *Dokl. Akad. Nauk SSSR* (rus). 142, 623-6 (1962).
- V.D.Prochuhan, Yu.V.Rud', Potential practical applications of II-IV-V₂ semiconductors Fiz.Tech.Polorovedn (rus) .12, 209 (1977)[Sov. Phys. Semiconductors 12 121 (1977)]
- 3. L.E. Halliburton et al, Electron paramagnetic resonance of a native acceptor in as-grown ZnGeP₂, *Appl. Phys. Lett.* **64**, 1615 (1994).
- R. Pandey , M.C.Ohmer, J.D.Gale, A theoretical study of native acceptors in CdGaAs₂, J. Phys.: Condens. Matter. 10, 5525 (1998).
- P.Zapol, R.Pandey, M.Ohmer, J. Gale, Atomistic calculations of defects in ZnGeP₂, J. Appl. Phys. 79, 671 (1996).
- 6. N.C.Giles, L.E.Halliburton, Native defects in the Ternary Chalcopyrites, *MRS Bulletin*. **23**(7), 37 (July ,1998).
- 7. F.A. Kroger. The chemistry of imperfect crystals (North-Holl, Publ. Co, Amsterdam, 1964).
- 8. S.P.Vul', V.D.Prochukhan, Yu.V.Shmartsev, Thermal defects in CdSnAs₂, *Dokl. Akad. Nauk SSSR*, *Tech. Phys.* (rus). **204**(5), 1094-6 (1972).
- B.H.Bairamov, V.Yu.Rud', Yu.V.Rud', Properties of Dopants in ZnGeP₂, CdGeAs₂, Ag-GaS₂, AgGaSe₂, MRS Bulletin.23(7), 41 (July ,1998).
- Ch. Dovletmuradov, A.Allanzarov, V.D. Prochukhan, Yu.V.Rud', M.Serginov, Effect of heat treatment on the electrical properties of p-CdGeAs₂, *Izv. Akad. Nauk Turkm. SSR.* Ser. Fiz.-Tekh, Khim. i Geol. Nauk (rus) 3, 106-8 (1972).

- 11.V.D.Prochukhan, About the behavior of the components of a lattice of compounds A²B⁴C⁵;₂, // Some problems of chemistry and physics of multinary semiconductors: Materials of a symposium (rus). 40 (UzhGU, Uzhgorod, 1970).
- 12.R.V.Masagutova, Research on the influence of lattice defects on the properties of monocrystals ZnGeP₂: Thesis of the cand. of chem. scien. (Leningrad, 1980).
- 13.V.D.Prochukhan, G.K.Averkieva, Effect of intrinsic lattice defects on the properties of compound A^{II}B^{iv}C^v₂, Teor. I Eksperim. Isslel. Slozhn. Poluprovodn. Soedinenii [Theoretical and experimental research on multinary semiconductor compounds](rus). 75-85 (Kishiniov, 1978).
- 14.F.P.Kesamanli, Yu.V.Rud', Wideband semiconductors A²B⁴C⁵;₂ with a chalcopyrite structure. *Ternary semiconductors and their application*. 39 (Shtiintsa, Kishiniov, 1979).
- 15.I.I.Tychina, Intrinsic lattice defects in the phosphides A²B⁴C⁵;₂. *Ternary semiconductors and their application*. 17 (Shtiintsa, Kishiniov, 1987).
- 16.V. S. Grigor'eva, V. D.Prochukhan, Yu. V.Rud', A. A.Yakovenko, Intrinsic donors in zinc germanium phosphide (ZnGeP₂) crystals, *Pis'ma Zh. Tekh. Fiz.* 1(3), 130-2 (1975). [Sov. Tech. Phys. Lett. 1(2) 61 (1975)]
- 17.G. A.Grishchenko, A.Sakalas, A.Sodeika, I. G.Tregub, Inversion of the conductivity type in zinc germanium phosphide (ZnGeP₂), *Liet. Fiz. Rinkinys*, **19**(6), 797-801 (1979).
- 18.A.Mamedov, M.Serginov, Lattice defects in the crystals CdSiAs₂. *Ternary semiconductors and their application*. 83 (Shtiintsa, Kishiniov, 1987).
- 19.L.V.Kradinova, V.D.Prochukhan, V.A.Radul, Effect of deviations from stoichiometry on the properties of ZnSnP₂ semiconductor. Nekot. Vop. Khim. Fiz. Poluprov. Slozhn. Sostava [Some problems of chemistry and physics of multinary semiconductors: Materials of a symposium (rus)]. 110-3 (UzhGU, Uzhgorod, 1970).
- 20.P.Zapol, R.Pandey, M.Seel, J.M.Recio, M.C.Ohmer, Density functional study of the structure, thermodynamics and electronic properties of CdGeAs₂, *J. Phys.: Condens. Matter.* 11, 4517 (1999).